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REPORT DOCUMENTATION PAGE

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1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS Unrestrictive	
2. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Unlimited	
AD-A228 876		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 00 1066	
4a. NAME OF PERFORMING ORGANIZATION Research Foundation of State University of NY	4b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC	
c. ADDRESS (City, State, and ZIP Code) 516 Capen Hall Buffalo, New York 14260		7b. ADDRESS (City, State, and ZIP Code) Building 410 Bolling Air Force Base, DC 20332	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (if applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-87-C0042	
c. ADDRESS (City, State, and ZIP Code) Building 410 Bolling Air Force Base, DC 20332		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO 61102F	PROJECT NO 2303
		TASK NO A3	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) (U) Design, Ultrastructure, and Dynamics of Nonlinear Optical Interactions in Polymeric Thin Films			
12. PERSONAL AUTHOR(S) Paras N. Prasad			
13a. TYPE OF REPORT Final Technical	13b. TIME COVERED FROM 3/1/87 TO 4/30/90	14. DATE OF REPORT (Year, Month, Day) 90-10-04	15. PAGE COUNT 25
16. SUPPLEMENTARY NOTATION			
COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Lt Col Larry P. David		22b. TELEPHONE (Include Area Code) (202) 767-4963	22c. OFFICE SYMBOL AFOSR/NC

FORM 1473, 84 MAR

83 APR edition may be used until exhausted.

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Sep 24 1990

Sponsored Programs
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FINAL REPORT

PROJECT:

Design, Ultrastructure, and Dynamics of Nonlinear
Optical Interactions in Polymeric Thin Films

SPONSOR:

USAFOSR

PERIOD:

March 1, 1987 to February 28, 1990

CONTRACT NO:

F4962087C0042

PRINCIPAL INVESTIGATOR:

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Accession For	
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1. SUMMARY

Under the present tenure of support by AFOSR we were able to develop a very comprehensive research program in the area of nonlinear optical effects in organic materials. This program covered microscopic theory of optical nonlinearity, design and synthesis of novel structures, materials processing for guided waves, measurements of optical nonlinearities and study of device processes. We made significant accomplishments in each topic as recognized by the number of invitations received to give talks at various international conferences. We have published extensively. In this progress report these accomplishments are listed separately under each topic. This description is followed by a list of publications supported by the current AFOSR contract and a list of invited talks during the tenure of this support.

1. Theory

We have used both classical anharmonic oscillator approach as well as ab-initio calculations to understand the microscopic nature of optical nonlinearities in organic structures. Our ultimate goal is to understand the structure-property relationship so that one may be able to predict structures with enhanced optical nonlinearities. The focus of our work has been on third-order optical nonlinearity.

We developed a simple model of coupled locally anharmonic oscillators which can be used to describe the optical nonlinearities in conjugated organic monomeric, oligomeric and polymeric structures.¹ We showed that the method can very readily be used to explain the dependence of the band gap, the polarizability, α , and the second hyperpolarizability, γ , as a function of the number of repeat units for the oligomers of thiophene and benzene. The results predicted by the coupled anharmonic oscillator model are in good agreement with those of the experimental studies on thiophene and benzene oligomers recently reported by our group. In addition, the predicted power dependences of orientationally averaged $\langle\alpha\rangle$ and $\langle\gamma\rangle$ on the number of repeat units were compared with those predicted by a free electron model, PPP methods, sum-over-states method and ab initio calculations.

Static polarizability and second hyperpolarizability tensors were computed for a series of polyenes, polyyenes and cumulenes by ab initio SCF theory.²⁻⁶ Numerically stable finite field (FF) calculations were achieved using polynomial fits of either energy or induced dipole moment as a

function of field strength. Fully coupled (FF) and uncoupled (SOS) ab initio SCF calculations, using identical small basis sets, were found to be in reasonably good agreement for polarizabilities but not for hyperpolarizabilities. The empirical function, Bn^λ , provides a qualitative description of how polarizability and hyperpolarizability varies with chain length, n , for moderately long chains. We modified the formula to take account of end effects in very short chains. Ab initio λ values are somewhat smaller than semiempirical values. Diffuse orbital basis functions are required for qualitatively correct hyperpolarizabilities of small conjugated pi systems. For example, the average second hyperpolarizability, Y , of ethylene is computed to be -13, 1.7 and 726 a.u. with STO-3G, 3-21G and augmented 3-21G basis sets, respectively, to be compared with the experimental value, 1500 a.u., of Ward and Elliott. We augment the valence set with diffuse s, p and two cartesian d sets, or subsets of these. The results are nearly insensitive to choice of valence set. We describe the use of a corresponding orbital analysis to aid in the interpretation of ab initio results obtained by either finite field or analytic derivative methods. The sigma orbital contribution to the longitudinal hyperpolarizability tends to partially cancel the larger pi contribution. Both contributions change sign in going from an acetylenic chain to the cumulene system. Polarizability and second hyperpolarizability are given by the first and third derivatives, respectively, of charge density with respect to field strength. A contour map of the first derivative density for an acetylenic chain is nearly periodic, corresponding to localized polarization of individual triple bonds. A map of the third derivative density does not exhibit this feature, corresponding to longer range charge shifts induced by the applied electric field.

With a goal to investigate the role of heavy atoms in determining optical nonlinearities, we conducted⁷ ab-initio calculations of polarizability, α , and first and second hyperpolarizabilities, B and Y for the haloform series CHX_3 where $X = F, Cl, Br, \text{ and } I$ using the Effective Core Potential (ECP) approach. The microscopic optical nonlinearities α , B and Y were calculated as the derivatives of the energy with respect to the electric field, with the energy determined by means of the Self-Consistent-Field approach (SCF), and nonlinearities calculated in the static field limit by means of the Coupled Perturbed Hartree-Fock (CPHF) formalism. To

test the usefulness of the ECP method, nonlinear optical responses for the lighter members of the series, CHF_3 and CHCl_3 , were computed by using both all electron and ECP calculations. The results are compared, and are found to be in excellent agreement. The effects of various basis sets and inclusion of diffuse and polarization functions are also examined to select a basis set which gives a good description of optical nonlinearities. The ECP technique is, then, used to calculate optical nonlinearities for CHBr_3 and CHI_3 . Although a very good agreement was found between the calculated and experimental polarizabilities for the haloform series, a rather poor agreement was obtained for the higher order polarizabilities. Possible sources of errors were discussed by us in order to elucidate this discrepancy.

In order to examine the importance of electron correlation, we conducted an ab-initio calculation of polarizability and second hyperpolarizability for the benzene molecule including electron-electron correlation.⁸ The finite field method was used. For each selected strength of the applied electric field the energy of the benzene molecule was calculated using the Self-Consistent Field method (SCF) as well as with its Moeller-Plesset correction in the second order (MP-2). Then the microscopic optical nonlinear responses were calculated by fitting both the SCF energy and the MP-2 energy to a polynomial in the field strength. We found that electron correlation significantly enhances the second hyperpolarizability. For the polarizability, our computed value showed an excellent agreement with the experimentally measured value. For the second hyperpolarizability, the computed value using MP-2 energy showed a reasonable agreement with that reported by the Electric Field Induced Second Harmonic (EFISH) generation but a poor agreement with the result of Degenerate Four Wave Mixing (DFWM). Finally, we also compared our ab-initio results with those previously reported using semi-empirical methods.

2. Design and Synthesis

The effort under this topic has been focused on making sequentially built and systematically derivatized structures with an objective that measurements of optical nonlinearities on these compounds will yield an insight into structure-property relationship. To investigate the dependence of the microscopic third-order optical nonlinearity χ on the number of

optical nonlinearities.¹¹ Our study indicates that the conjugations does not really carry through the metal. The γ value appears to be determined by the Π -conjugation through the organic segment.

3. Materials Processing

The research under this category has focussed on the preparation of optical quality films and characterization by using structural and spectroscopic techniques. Ultrathin films with a monolayer resolution have been prepared using both the Langmuir-Blodgett method and the electrochemical polymerization techniques. Thin films of optical waveguide dimensions were made by using solution casting techniques such as spin-coating and doctor blading. To a very limited extent vacuum deposition has also been used. The objective has been to improve on the optical quality of these films for guided wave or surface-plasmon nonlinear optics.

Molecular assemblies prepared by the Langmuir-Blodgett technique provide useful structures to probe structure-property relationships for nonlinear optical processes. We developed a comprehensive research program in which we studied the Langmuir-Blodgett films of optically nonlinear organic structures. The films were carefully characterized by a variety of surface and spectroscopic techniques. Both second and third order processes were investigated. We have successfully formed monolayer and multilayer films of several phthalocyanines and characterized them by u.v. visible spectroscopy, ellipsometry and quartz-crystal microbalance method.^{12,13} The layer-to-layer deposition was found to be uniform for the number of layers studied (~40). An interesting phthalocyanine, Si-phthalocyanine, SiPc(OSiMePhOH)_2 - was synthesized in our laboratory following published procedures. It forms a nice condensed L-B film.¹³

Monolayer films of poly-3-BCMU were shown to form at the air-water interface, the surface pressure/area per residue (π/A) isotherms of which exhibit a horizontal plateau indicative of a phase change occurring on compression.¹⁴ Langmuir-Blodgett monolayer films, transferred while proceeding through this region, have visible absorption spectra indicating a conformational change from an amphipathic yellow to a nonamphipathic blue form having increased π -electron conjugation. A thermodynamic analysis of the temperature dependency of the compressional onset of the plateau (π_c), interpreted in terms of a corrected two-dimensional analogue of the

Clapeyron equation, shows a slightly exothermic transition. A comparison of isotherms obtained both by continuous compression and by a stepwise "equilibrium" method shows considerable relaxation can take place at areas per residue less than 100 \AA^2 . This was interpreted as reflecting the pronounced reorganization required for the highly ordered blue conformation to completely form. Multilayers of poly-3-BCMU and poly-4-BCMU transferred at different areas per residue show visible absorption spectra reflecting the different degrees of conformational order of the monolayer films from which they were fabricated. When monolayers of poly-4-BCMU and poly-3-BCMU are sandwiched, an alternation multilayer is formed in which the highly ordered blue conformation is forced to assume the slightly less ordered red conformation of poly-4-BCMU.

Studies conducted by our research group have revealed that soluble polydiacetylenes, poly-n-BCMU (the coefficient, n, simply represents the number of methylene units in the side chain), can be manipulated in the monolayer film to control the polymer conformation, order and π -conjugation. We have investigated poly-3-BCMU and poly-9-BCMU which undergo a monolayer yellow form-to-bilayer blue form transition while the poly-4-BCMU discussed above shows a monolayer yellow form to a bilayer red form transition. The blue form is the most conjugated structure. The π -conjugation strongly influences the optical nonlinearity. Therefore, by controlling the effective conjugation by the L-B technique, one can judiciously tune the optical nonlinearity. In addition to the pressure dependent monolayer to bilayer transitions, effective π conjugation can be changed by virtue of the fact that all the monolayers can be polymerized by u.v. light.

The 9-BCMU multilayer films show more subtle differences in the degree of order and conjugation when prepared differently.¹³ The solution cast film when polymerized by u.v. light shows the least order ($\lambda_{\text{max}} = 635 \text{ nm}$) for a blue form. When a 9-BCMU monomer monolayer film is polymerized at the air-water interface and then transferred to a substrate it shows a greater degrees of order and conjugation ($\lambda_{\text{max}} = 645 \text{ nm}$). The most ordered polymerized multilayer is obtained when the monomer is first transferred as a multilayer and then polymerized ($\lambda_{\text{max}} = 655 \text{ nm}$).

Surface plasmon wave spectroscopy was successfully used to study the monolayer-bilayer transition in poly-4-BCMU and poly-3-BCMU polydiacetylene Langmuir-Blodgett films.¹⁵ The linear refractive index and the thickness

were obtained for the monolayer yellow and bilayer red forms of poly-4-BCMU. Surface plasmon coupling using resonance enhancement was found to sufficiently enhance the Raman scattering, so Raman spectra of the monolayer films could be obtained with a relatively small laser intensity of a few milliwatts. The differences in the C=C and C C vibrational stretching frequencies of the monolayer yellow and the bilayer red films were observed arising from the difference in the effective conjugation for the two forms.

Monolayer film formation at the air/water interface was investigated for both electrochemically and chemically prepared poly(3-dodecylthiophene) using surface pressure-molecular area isotherms.¹⁶ Only the electrochemically prepared polymer formed a stable monolayer, which was successfully transferred using the horizontal lifting method. The transferred Langmuir-Blodgett films were characterized by u.v.-visible spectroscopy and quartz crystal microbalance measurements.

In order to study the structural correlation from layer to layer we have successfully used a combination of the quartz-crystal microbalance method and u.v.-visible spectroscopy.^{12,13,16} A quartz-crystal microbalance utilizing the change in the resonance frequency upon the film deposition provides a convenient method of determining the mass of the film. Therefore, the uniformity of the mass transfer can be determined from the layer dependence. In the case of a uniform mass transfer, a linear relation will be obtained between the number of layers and the change in the frequency. The u.v.-visible spectra in the linear absorption regime would also yield a linear dependence of the absorbance as a function of the number of layers, provided the structural correlation from layer-to-layer is maintained. The results of the quartz-crystal microbalance and the u.v.-visible spectral studies for L-B films of a macrocycle, tetrakis butyl phenoxy phthalocyanine show a linear relation in each case indicating a uniform transfer from layer-to-layer with the same molecular structure.^{12,13} In contrast, the results on the L-B films of poly (3-dodecyl-thiophene) reveal a uniform mass transfer (linear relation between the frequency change in the quartz-crystal microbalance experiment and the number of layers), but the structural correlation from layer-to-layer changes around the tenth layer as evidenced by the change of slope of the absorbance as a function of the number of deposited layers.¹⁶

Monolayer film formation was observed for a liquid crystalline copolymer containing a second-order non-linear optical side chain.¹⁷ The films were characterized on the aqueous subphase by a pressure-area per monomer unit isotherm and successfully transferred onto a glass substrate by the horizontal lifting method. The transferred Langmuir-Blodgett monolayers were characterized by surface plasmon resonance, attenuated total reflection-IR (ATR-IR) and UV-visible spectroscopy. The surface plasmon resonance study revealed the Langmuir-Blodgett films transferred at 5 dyn cm⁻¹ to be uniform but not those at 10 and 15 dyn cm⁻¹. The theoretical fit of the surface plasmon results for the monolayer Langmuir-Blodgett films transferred at 5 dyn cm⁻¹ coupled with ellipsometric results on a solution-cast film yielded the values for the refractive index and the thickness of the monolayer. ATR-IR and UV-visible spectra show that the copolymer has similar conformations in the monolayer and bulk states.

We investigated electrochemically polymerized films. Our work showed that by using a modified gold working electrode, the surface plasmon technique can successfully be used to obtain information on the optical constants and the film thickness of electropolymerized films.¹⁸ Polyazulene films deposited at three different surface charge densities were investigated in the oxidized and corresponding reduced forms. Our result shows that the refractive index, and hence the dielectric constant at 632 nm, is complex, the imaginary part being larger for the oxidized form compared to that for the corresponding reduced form. Thickness determination shows that its relationship with the amount of charge is qualitatively similar to that reported for polypyrrole. The film thickness measurement reveals a shrinkage in going from the oxidized to the reduced form as the counter anions are removed.

We were successful in making waveguides of several polymers and characterizing their optical properties. We conducted measurements of the refractive indices of poly-4BCMU films and reported the fabrication of an efficient integrated optical coupler.¹⁹ The refractive index measurements were performed in the visible and near infrared using blazed-grating couplers. The analysis led to the optimization of a blazed-grating input coupler with a coupling efficiency larger than 45% at 1.064 μ m.

We reported the observation of a large birefringence in a as-cast unoriented film of poly-p-phenylene vinylene, a material which has a large

third-order nonlinear optical susceptibility.²⁰ A wave guide technique in the TE and TM polarizations was used to obtain the in-plane and out-of-plane refractive indices at several wavelengths. At 633 nm the measured refractive index values are: $n_{TE} = 2.085$, $n_{TM} = 1.612$. No dependence of the in-plane refractive index on the direction of film spreading is found indicating an in-plane isotropic behavior. No anomalous dispersion of refractive index is found in the wavelength range 633 nm to 1064 nm.

We used sol-gel processing to fabricate planar waveguides and characterize their properties.²¹ In this regard our objective has been to make low loss nonlinear optical waveguides of composite materials. We have a remarkable success in developing a special sol-gel process route by which we are able to make a good optical quality composite of the sol-gel silica and the poly-p-phenylene vinylene (PPV) polymer. We are able to make without phase separation a composite which contains a large composition of the nonlinear polymer PPV. The waveguide losses are significantly lower than what is found for the pure PPV waveguides. A patent has been filed for the processing of this composite.

4. Experimental Studies of Optical Nonlinearities

Monolayers of several diacetylene monomers and polymers spread at the air-water interface were studied^{22,23} using optical second-harmonic generation (SHG) and third-harmonic generation (THG). Owing to the centrosymmetry of the diacetylene core, SHG from these molecules arises mainly from their side groups. THG from a single monolayer of polydiacetylene was reported, to our knowledge, for the first time - the THG signal (in reflection) arising from the polydiacetylene monolayer is several times larger than that from the water subphase. THG was observed both when a polymer monolayer was spread directly and when a monomer monolayer was UV polymerized on the water surface. Values of the third-order nonlinearity of polydiacetylenes derived from these measurements are in agreement with earlier studies.

With a goal to understand the structure-property relationship for third-order microscopic optical nonlinearity, we have investigated the nonlinearities of a number of sequentially built and systematically derivatized π -conjugated structures using degenerate four-wave mixing. A systematic study of the dependence of the band gap, the linear optical

susceptibility, the polarizability α , and the second hyperpolarizability γ , on the number of repeat unit was conducted for the thiophene series from monomer to hexamer.⁹ The linear optical susceptibilities for oligomers were determined from the refractive index measurements on vacuum deposited films using the m lines technique. The orientationally averaged polarizabilities $\langle\alpha\rangle$ were measured from refractive index measurements of THF solutions. The orientationally averaged second hyperpolarizabilities $\langle\gamma\rangle$ were measured by degenerate four-wave mixing studies of THF solutions. The validity of the Lorentz-Lorenz approximation was tested and found to be satisfactory. The experimental values of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ for thiophene and $\langle\alpha\rangle$ for bithiophene are found to be in qualitative agreement with those obtained by a recent ab initio calculation which used the finite field method and included diffuse polarization functions. The experimentally observed dependence of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ on the number N of the thiophene repeat unit is compared with that predicted by a free electron model, PPP methods, and the ab initio calculations. For the case of polarizability, the repeat unit dependence is in good agreement with that predicted by the ab initio calculations but for the case of second hyperpolarizability, the agreement is not as good. To examine the nature of effective conjugation, we measured the third-order microscopic nonlinearities, γ , for several para poly-phenyls and compared the dependence on the number of repeat units with that observed in the α -thiophene oligomers.¹⁰ Our results show that the limiting conjugation length in each conjugated series may be different, it becomes much shorter for poly-phenyls than that for polythiophenes. Systematically derivatized α -terthiophene structures have also been investigated. The substitution of a pyrrole or a benzene unit in the place of the central thiophene ring in the α -terthiophene structure reduces the γ value. The substitution of polarizable iodine atoms at the end α positions of γ -terthiophene increases the γ value. Even larger increases in the γ values are observed with the mononitro- and dinitro- substitutions at the α positions in the α -terthiophene structure. Possible theoretical reasons for such changes in the γ values for derivatized structures have been discussed.

The third-order nonlinear optical susceptibility was investigated at wavelengths of 602 and 580 nm for a 10:1 stretch-oriented uniaxial film of poly (p-phenylene vinylene) using femtosecond degenerate four wave mixing.²⁴ A relatively large $\chi^{(3)}$ with a subpicosecond response was observed. A large

anisotropy in the $\chi^{(3)}$ value was found, the largest component of $\chi^{(3)}$ ($= 5 \times 10^{-10}$ esu) being along the draw direction.

To investigate the effect of vibrational resonance on optical nonlinearity we conducted the first study of both time-resolved and frequency domain coherent Raman scattering in a conjugated polymer, specifically a soluble polydiacetylene called poly-4-BCMU.²⁵ Both the CARS and CSRS spectra were recorded at room temperature and at 4 K in the region of -C=C- stretch on a ~12 μ m thick film of poly-4BCMU in the red amorphous form. The relevant CSRS spectra of the blue crystalline form were also reported. Frequency domain study reveals the vibrational resonance frequency to be independent of the polymer molecular weight in the red form, but different for the blue and red form. The line shapes are asymmetric, but do not seem to fit the predictions of a simple model involving dominant two-photon resonance contributions. The observed vibrational dephasing in the time-resolved study is very fast at both room temperature and 4 K, being within the time-resolution available. From the combined analysis of the frequency domain and time-resolved studies at both room temperature and 4 K, an inhomogeneous mechanism of dephasing was inferred. The inhomogeneous dephasing arises from simultaneous coherent excitation of a distribution of vibrational frequencies originating from a distribution of polymer conjugation length.

Electronically resonant third-order optical nonlinearity, in several photoresponsive polymers were studied by picosecond and femtosecond degenerate four-wave mixing to investigate the role of photoexcited charge carriers.²⁶ Both the magnitude and the response time of the observed optical nonlinearities seem to vary over a wide range. In the case of a solution processable polyacetylene-polymethyl methacrylate graft co-polymer, the observed resonant $\chi^{(3)}$ has an extremely fast initial decay and is consistent with what can be expected from the intrachain soliton dynamics.

Resonant third-order nonlinear optical susceptibility $\chi^{(3)}$ of poly-N-vinyl carbazole: 2,4,7-trinitrofluorenone composite polymer photoconductor was measured at 602 nm for various compositions by picosecond degenerate four-wave mixing.^{26,27} The origin of effective third-order nonlinearity of this system is attributed to the charge-transfer excitation which creates thermalized correlated electron-hole pairs. The optical nonlinearity of this polymeric system is characterized by a long relaxation time of hundreds

of picoseconds. A progressive enhancement of the signal intensity and hence effective $\chi^{(3)}$ accompanied by an increase in the decay rate of the degenerate four-wave mixing signal has been observed with an increase in the mole fraction of trinitrofluorenone.

In the case of an electrochemically formed polymer, specifically polythiophene, we observed a relatively large $\chi^{(3)}$ with, again, a very fast initial decay in subpicoseconds consistent with the intrachain polaronic processes.^{26,28} An in situ study of the nonlinear optical behavior as a function of electrochemical redox cycle showed a drastic reduction of the overall $\chi^{(3)}$ as the film is oxidized. The third-order optical susceptibility of undoped poly(3-dodecylthiophene) was found to be $\chi^{(3)} \sim 10^{-9}$ esu, large enough to allow the first reported observation of a degenerate four-wave mixing signal from ultrathin Langmuir-Blodgett films of this material.¹⁶ In situ iodine-doping studies of UV-Visible absorption, electrical conductivity and third-order nonlinear optical susceptibility were carried out. Upon doping, the conductivity changed by more than eight orders of magnitude but the $\chi^{(3)}$ value decreased to within ten percent of the original value.

We also studied the resonant $\chi^{(3)}$ behavior of L-B films of several phthalocyanines.^{4,12,13} Again, the nonlinearity was sufficiently large to observe the degenerate four-wave mixing signal even from a monolayer. The value of $\chi^{(3)}$ is $> 10^{-9}$ esu with response being in several picoseconds. Both the magnitude of $\chi^{(3)}$ and the decay of the signal was found to be dependent on the laser intensity. We assign the intensity dependent decay to the presence of bimolecular processes (exciton-exciton annihilation).¹³

We used a novel approach using simultaneous monitoring of temporal behavior of the usual phase conjugate signal and the second-order diffraction produced in a degenerate four-wave mixing experiment to obtain information about dynamics of resonant third-order nonlinear optical processes.²⁹ The second order diffraction is interpreted as arising from the presence of the appropriate Fourier component of the excited state grating. The higher Fourier components are expected to be generated in the presence of such excited state processes as bimolecular decay, two-photon absorption, saturation of absorption and diffusion of excitation.

Third order nonlinear optical properties of an organic dye: perylene tetracarboxylic dianhydride were studied by this approach using

subpicosecond degenerate four-wave mixing at a wavelength of 602 nm. The dye was found to exhibit a strong resonant nonlinear effect with an effective $\chi^{(3)}$ of $\approx 2 \times 10^{-10}$ esu. The decay of the phase conjugate signal is power dependent and can be theoretically simulated by using a combination of monomolecular and bimolecular decay laws. The temporal behavior of the phase conjugate signal and the second order diffraction was investigated at different intensities. The observed characteristics are well simulated by using a dominant bimolecular decay mechanism at higher excitation density.

The picosecond laser-induced transient grating technique was used to determine the elastic constants of a predominantly uniaxial film of a rigid-rod polymer, poly (benzobisoxazole).³⁰ By adjusting the grating angle, ultrasonic phonons in the frequency range 0.4-2 GHz were generated and their in-plane speed in various directions was measured. The speed was found to be independent of the phonon frequency in the range of frequency studied. The general Christoffel equation was used to fit the observed anisotropy of the acoustic velocity. This fit conveniently yielded various elastic moduli demonstrating the application of picosecond laser-induced transient grating methods for obtaining both longitudinal and shear components of elastic constants for an anisotropic medium.

The picosecond transient grating technique was also used to obtain acoustic speed as a function of film orientation in a uniaxially stretch-oriented film of poly (vinylidene difluoride) at liquid nitrogen temperature.³¹ By the analysis of acoustic speed anisotropy using the general Christoffel equation, we have obtained both the longitudinal and shear components of the elastic moduli of the film. Our results are in qualitative agreement with those of a published Brillouin scattering study.

5. Device Processes

Our study under this category focused on the investigation of nonlinear optical processes in waveguides and fibers.

Optical bistable behavior in a novel scheme using a quasi-waveguide interferometer with the third-order nonlinearity of the guiding film of a soluble polydiacetylene (poly-4BCMU) was demonstrated.³² This device shows an input-output behavior analogous to that of a nonlinear Fabry-Perot etalon. The value of $\chi^{(3)}$ for poly-4BCMU estimated from the switching power

is considerably higher than the earlier reported nonresonant values measured by other methods.

We reported the first clear demonstration³³ of intensity-dependent phase shift due to electronic nonlinearity in a nonlinear polymer waveguide in which propagation distances over 5 cm were achieved with total attenuation of $\sim 1.2 \text{ cm}^{-1}$. Intensity-dependent coupling angle, intensity-dependent coupling efficiency, and limiter action behavior were observed in the polyamic acid waveguide using grating excitation with 400 fs, 80 ps, and 10 ns pulses. A nonlinear grating coupler analysis identifies the subpicosecond and picosecond processes with electronic nonlinearity, but the dominant effect in the nanosecond experiment is due to thermal nonlinearity derived from weak absorptions. The magnitude and sign of n_2 of electronic nonlinearity were measured.

By using a long interaction length (250 cm) provided by a liquid-core multi-mode hollow fiber, we have observed novel nonlinear optical effects derived from orientational nonlinearities.³⁴⁻³⁷ Novel superbroadening ($>100 \text{ cm}^{-1}$) of the stimulated scattering added to the pump line (Rayleigh) and the stimulated Raman scattering lines have been observed for several anisotropic liquids (CS_2 , benzene).^{34,35} To explain these effects, we have proposed a photon scattering model of Rayleigh-Kerr optical effect and Raman-induced optical Kerr effect. For device applications, we have demonstrated the application of this broadening to conveniently achieve a very high amplification of a broad band optical signal.³⁶

Additional publications are from 38 to 47.

2. PUBLICATIONS RESULTING FROM AFOSR SUPPORT

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14. "Monolayer and Langmuir-Blodgett Multilayer Surface and Spectral Studies of Poly-3-BCMU" J. E. Biegajski, D. A. Cadenhead and P. N. Prasad, Langmuir 4, 689-693 (1988).
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18. "Surface Plasmon Study of Electrochemically Prepared Polymers: Polyazulene" X. Huang, M. T. Zhao, L. Janiszewska and P. N. Prasad, Synthetic Metals 24, 245 (1988).
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23. "A Study of Diacetylene Monomer and Polymer Monolayers Using Second- and Third- Harmonic Generation" G. Berkovic, R. Superfine, P. Guyot-Sionnest, Y. R. Shen and P. N. Prasad, J. Opt. Soc. Am. B 5, 668 (1988).
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25. "Picosecond Time-resolved and Frequency Domain Coherent Raman Scattering Study of Conjugated Polymeric Films: A Soluble Polydiacetylene, poly-4-BCMU." J. Swiatkiewicz, X. Mi., P. Chopra and P. N. Prasad, J. Chem. Phys. 87, 1882 (1987).
26. "Resonant Nonlinear Optical Processes and Charge Carrier Dynamics in Photoresponsive Polymers" P. N. Prasad, J. Swiatkiewicz and J. Pfleger, Molecular Crystals and Liquid Crystals 160, 53 (1988).
27. "Picosecond Degenerate Four Wave Mixing Study of Nonlinear Optical Properties of the Poly-n-Vinyl Carbazole 2,4,7-trinitrofluorenone Composite Polymer Photoconductor" S. K. Ghoshal, P. Chopra, B. P. Singh, J. Swiatkiewicz and P. N. Prasad, J. Chem. 90, 5078 (1989).
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29. "Dynamics of Resonant Third-Order Optical nonlinearity in Perylene Tetracarboxylic Dianhydride Studied by Monitoring First and Second Order Diffractions in Subpicosecond Degenerate Four Wave Mixing" M. Samoc and P. N. Prasad, J. Chem. Phys. 91, 6643 (1989).
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35. "A Novel Nonlinear Optical Effect: Stimulated Raman-Kerr Scattering in a Benzene Liquid-Core Fiber" G. S. He, R. Burzynski and P. N. Prasad, *J. Chem. Phys.* (in Press).
36. "Stimulated Amplification of a Broad-Band Optical Signal Through a Benzene-Core Fiber System Pumped by Ultra-Short Laser Pulses" G. S. He, G. C. Xu, R. Burzynski and P. N. Prasad, *Optics Commun.* 72, 397 (1989).
37. "Stimulated Rayleigh-Kerr Scattering in a CS₂ Liquid-core Fiber System" G. S. He and P. N. Prasad, *Optics Commun.* 73, 161 (1989).
38. "Nonlinear Optical Effects in Thin Organic Polymeric Films" P. N. Prasad, *Thin Solid Films* 152, 275 (1987).
39. "Phonon Spectroscopy of Organic Solid State Reactions" P. N. Prasad in Organic Solid State Chemistry ed. G. R. Desiraju. Elsevier (Amsterdam, 1987) p. 117.
40. "Organic Polymers As Nonlinear Optical Materials" P. N. Prasad, *Optics News* 13, 34 (1987).
41. "Nonlinear Optical Effects in Organic Molecules and Polymers - Theory, Measurements and Devices" P. N. Prasad in Nonlinear Optical Materials, Proceeding of the International Congress on Optical Science and Engineering. Hamburg, Germany, SPIE., proceeding vol. 1017, p. 2 (1989).
42. "Nonlinear Optical Properties of Halomethanes Studies by Subpicosecond Degenerate Four Wave Mixing and Electric-field Induced Second Harmonic Generation" A. Samoc, M. Samoc, P. N. Prasad, C. Willand, and D. J. Williams, submitted for publication to *J. Phys. Chem.*

43. "Molecular Weight and Comparative Studies of Poly-3- and Poly-4-BCMU Monolayers and Multilayers" J. E. Biegajski, R. Burzynski, D. A. Cadenhead and P. N. Prasad, *Macromolecules* 23, 816 (1990).
44. "Photonics and Nonlinear Optics - Materials and Devices" in Proceedings of NATO Advanced Study Institute at Spetses Island, Greece, June 12-23, 1989, Ed. R. M. Metzger (to be published).
45. "Langmuir-Blodgett Films for Nonlinear Optics" in Proceedings of NATO Advanced Study Institute at Spetses Island, Greece, June 12-23, 1989, Ed. R. M. Metzger (to be published).
46. "Stimulated Rayleigh-Kerr and Raman-Kerr Scattering in a Liquid-core Hollow Fiber System" G. S. He and P. N. Prasad, *Fiber and Integrated Optics*.
47. "Anisotropy of the Linear and Third-order Nonlinear Optical Properties of a Stretch-Oriented Poly(2,5-dimethoxy paraphenylene vinylene)" J. Swiatkiewicz, P. N. Prasad, F. E. Karasz, M. A. Druy and P. Glatkowski, *Appl. Phys. Lett.* 56, 892 (1990).

3. INVITED TALKS AND WORKSHOPS ON RESEARCH SUPPORTED BY AFOSR

1. Wright-Patterson Air Force, Polymer Branch, Dayton, OH, March 9, 10, 1987, two days Tutorial on "Organic Nonlinear Optics".
2. Western New York American Chemical Society Jointly Sponsored with the Analytical group, Buffalo, NY, March 17, 1987.
 "Non-linear Optical Effects in Ultra Thin Polymeric Films: Concepts and Device Applications".
3. E. I. Dupont de Nemours Company, Wilmington, DE, March 23, 1987
 "Nonlinear Optical Effects in Thin Polymeric Films".
4. New York University, Department of Chemistry, New York, NY, April 3, 1987
 "Nonlinear Optical Effects in Polymeric Films and Spectral Diffusion in Orientationally Disordered Organic Solids".
5. Spring 1987 ACS Meeting, Denver, Symposium on Electroactive Polymers, April 6, 1987.
 "Design, Ultrastructure and Dynamics of Nonlinear Optical Effects in Polymeric Films".
6. University of Arizona, Optical Sciences Center, Tucson, AZ, April 10, 1987.
 "Nonlinear Optical Effects in Organic Polymeric Films".
7. Materials Research Council/DARPA Workshop on Nonlinear Optical Materials, LaJolla, CA, July 23, 1987.
 "Nonlinear Optical Effects in Polymeric Films".
8. SPIE - The International Society for Optical Engineering, 31st Annual International Technical Symposium on Optical and Optoelectronic Applied Science and Engineering, August 20, 1987.
 Tutorial Lecture on "Molecular Engineering of Ultrathin Organic Polymeric Films with the Langmuir-Blodgett Technique: Molecular Designs and Device Application".
9. NSF Chemistry/Chemical Engineering Planning Workshop on Chemical Processing of Advanced Materials for Information Storage and Handling, Washington, D.C., September 14-15, 1987.
10. Symposium on Electroresponsive Polymers, Brookhaven National Laboratory, October 5, 1987.
 "Nonlinear Optical Effects in Polymeric Films".
11. University of West Virginia, Department of Chemistry, Morgantown, WV, October 21, 1987.
 "Nonlinear Optical Effects in Organic Molecules and Polymers".

12. The Materials Research Society 1987 Fall Meeting, Boston, MA, December 3, 1987.
 "Nonlinear Optical Properties of Polymers".
13. National Materials Advisory Board, Committee on Liquid Crystalline Polymers, National Academy of Sciences, Washington, DC 20418.
 "Nonlinear Optical Effects in Liquid Crystalline Polymers".
14. SPIE - The International Society for Optical Engineering, Meeting, Los Angeles, CA, January 10, 1988.
 Tutorial Lecture on "Nonlinear Optical Materials".
15. SPIE - The International Society for Optical Engineering, Meeting, Los Angeles, CA, January 12, 1988, Symposium on Multifunctional Materials.
 "NLO Interactions in Langmuir-Blodgett Organic Semiconductor Heterostructures".
16. Johns Hopkins University, Department of Materials Science, Baltimore, MD, March 2, 1988.
 "Picosecond and Femtosecond Degenerate Four Wave Mixing Study of Nonlinear Optical Effects and Mechanical Properties of Polymer Films".
17. University of Nevada at Reno, Department of Chemistry, Reno, NV, March 23, 1988.
 "Nonlinear Optical Effects in Organic Molecules and Polymers".
18. Iowa State University, Department of Chemistry, Ames, IA, March 25, 1988.
 "Nonlinear Optical Effects in Organic Molecules and Polymers".
19. AFOSR Contractor Review of Nonlinear Optical Polymers. National Academy of Sciences, Washington, DC, April 21, 1988.
20. A Topical Workshop on Organic and Polymeric Nonlinear Optical Materials, Sponsored by Division of Polymer Chemistry, American Chemical Society, May 16, 1988, Virginia Beach, VA.
 "Nonlinear Optical Effects in Polymeric Films".
21. US-UK Optical Glass and Macromolecular Materials Seminars, June 17, 1988, Pitlochry, Scotland.
 "Charge Carrier Dynamics and Nonlinear Optical Processes in Organic Langmuir-Blodgett Films".
22. NATO Advanced Research Workshop on "Polymers for Nonlinear Optics" June 24, 1988, Sophia Antipolis, France.
 "Ultrafast Nonlinear Optical Processes in Organic Polymers".
23. International Conference on "Organic Materials for Nonlinear Optics" June 29, 1988, Oxford, England.
 "Ultrafast Third Order Nonlinear Optical Processes in Organic Polymers".

24. Gordon Conference on Dielectric Phenomena, July 27, 1988, New Hampshire.
"Recent Advances in the Field of Nonlinear Optics".
25. SPIE - The International Society for Optical Engineering, 32nd Annual International Technical Symposium on Optical and Optoelectronic Applied Science and Engineering, San Diego, CA, August 16, 1988.
Tutorial Lecture on "Introduction to Nonlinear Optical Materials".
26. SPIE - the International Society for Optical Engineering, 32nd Annual International Technical Symposium on Optical and Optoelectronic Applied Science and Engineering, San Diego, CA, August 17, 1988.
Tutorial Lecture on "Molecular Engineering of Ultrathin Organic Polymeric Films with the Langmuir-Blodgett Technique: Molecular Designs and Device Applications".
27. Topical meeting on Nonlinear Optical Properties of Materials, Optical Society of America, Troy, NY, August 23, 1988.
"Optical Nonlinearities of Polymers".
28. Trinity College, Department of Physics, Dublin, Ireland, September 16, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers".
29. The International Congress on Optical Science and Engineering, Hamburg, Germany, September 21, 1988.
Tutorial Lecture on "Introduction to Nonlinear Optical Materials".
30. The International Congress on Optical Science and Engineering. Hamburg, Germany, September 22, 1988.
Plenary Lecture on "Nonlinear Optical Effects in Organic Molecules and Polymers - Theory, Measurements and Devices".
31. Technical University of Munich, Department of Physics, Germany, September 27, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers".
32. National School on Nonlinear Optics, Brallo (Milan), Italy, September 30, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers".
33. NTT Opto-Electronics Laboratories, Tokai, Naka-gun, Ibaraki, Japan, November 9, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers".
34. Research Institute for Polymers and Textiles, Tsukuba, Japan, November 10, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers - Theory, Measurements and Devices".

35. The University of Tokyo, Department of Physics, Tokyo, Japan, November 11, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers - Theory, Measurements and Devices".
36. Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan, November 14, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers - Theory, Measurements and Devices".
37. Materials Research Society Fall Meeting, Boston, MA, December 2, 1988.
"Nonlinear Optical Properties of Rigid Rod Polymers and Model Compounds".
38. Syracuse University, Department of Chemistry, Syracuse, NY, December 13, 1988.
"Nonlinear Optical Effects in Organic Molecules and Polymers - Theory, Measurements and Devices".
39. SPIE - The International Society for Optical Engineering Meeting, Los Angeles, CA, January 17, 1989. Symposium on Multifunctional Materials.
"Nonlinear Optics of Langmuir-Blodgett Films".
40. SPIE - The International Society for Optical Engineering Meeting, Los Angeles, CA, January 19, 1989. Tutorial Lecture.
"Introduction to Nonlinear Optical Materials".
41. Fourth International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Tucson, AZ, February 21, 1989.
"Nonlinear Optical Processes in Polymers and Sol-gel Composites".
42. Electric Power Research Institute Workshop on "Polymers in the Generation, Storage, Transmission and Distribution of Electric Power", Baltimore, Maryland, March 15, 1989.
"New Developments in the Nonlinear Optical Properties of Polymers and Their Applications: The Technology of Advanced Polymer Photonics".
43. American Physical Society Meeting, Division of High Polymer Physics Symposium, St. Louis, MO, March 24, 1989.
"Nonlinear Optical Effects in Organic Molecules and Polymers - Theory, Measurements and Devices".
44. ACS Spring Symposium on Nonlinear Optics and Materials, Rochester Section, Rochester, NY, April 19, 1989.
"Third-Order Nonlinear Optical Processes in Organic Molecules and Polymers."

45. International Congress on Optical Science and Engineering, Paris, France, April 24, 1989. A one day Tutorial on
"Introduction to Nonlinear Optical Materials".
46. Quantum Electronics and Laser Science Conference '89, Baltimore, MD, April 24, 1989.
"Dynamics of Third-Order Nonlinear Processes in Organic Molecules and Polymers" M. Samoc, J. Swiatkiewicz and P. N. Prasad.
47. University of Nantes, Institute of Physics and Chemistry of Materials, Nantes, France, April 25, 1989.
"Nonlinear Optical Effects in Conjugated Polymers".
48. University of Lille, Department of Chemistry, Lille, France, April 26, 1989.
"Time-Resolved Studies of Nonlinear Optical Processes in Organic Molecules and Polymers".
49. University of Lille, Department of Physics, Lille, France, April 27, 1989.
"Nonlinear Optical Effects in Organic Crystals and Polymers".
50. Allied-Signal, Morristown, NJ, May 24, 1989.
"Nonlinear Optical Effects in Polymers".
51. The New York Academy of Sciences, Section of Polymer Science, New York, NY, May 24, 1989.
"Nonlinear Optical Properties of Polymers and Their Applications: The Technology of Advanced Polymers Photonics".
52. University of Wyoming, Department of Chemistry, Laramie, WY, June 13-16, 1989. Five Lectures under 1989 Summer Lecture Series in Chemistry
"Nonlinear Optical Effects - Theory, Materials, Measurements and Devices".
53. NATO Advanced Study Institute on "Lower-Dimensional Systems and Molecular Devices" Spetses Island, Greece, June 19, 1989.
"Photonics and Nonlinear Optics - Materials and Devices".
54. NATO Advanced Study Institute on "Lower-Dimensional Systems and Molecular Devices" Spetses Island, Greece, June 21, 1989.
"Langmuir-Blodgett Films for Nonlinear Optics".
55. International Summer School on Nonlinear Optics, Aalborg, DENMARK, July 31 - August 4, 1989. Two lectures on
"Nonlinear Optical Effects in Organic Materials".

56. SPIE - The International Society for Optical Engineers, 33rd Annual International Technical Symposium on Optical and Optoelectronic Applied Science and Engineering, San Diego, CA, August 7, 1989. Tutorial Lecture "Introduction to Nonlinear Optical Materials".
57. US-UK Optical Glass and Macromolecular Materials Workshop, Ilkley, U.K., August 29-31, 1989.
"Novel Electroactive and Nonlinear Optical Heterostructures".
58. Nonlinear Optical Polymers Contractors Conference, Long Beach, CA, September 24-26, 1989.
"Experimental and Theoretical Studies of Nonlinear Optical Effects in Molecular Materials and Polymers".
59. American Chemical Society, Live Satellite Television course, November 17, 1989.
"Nonlinear Optical Properties of Polymers".
60. Materials Research Society, Fall Meeting 1989. Boston, MA, November 30, 1989.
"Novel Electroactive and Nonlinear Optical Heterostructures".
61. Pacific Basin Chemical Congress, American Chemical Society, Dec. 17, 1989, Symposium on Polymers for Photonics.
"Studies of Third-Order Nonlinear Optical Effect in Sequentially Built and Systematically Derivatized Organic Structures".
62. Pacific Basin Chemical Congress, American Chemical Society, Dec. 17, 1989, Symposium on Time-Resolved Vibrational and Other Molecular Dynamical Processes.
"Dynamics of Nonlinear Optical Processes in Organic Molecules and Polymers".
63. Joint United States - Israel Workshop on Light Energy Conversion: Natural Systems and Synthetic Materials, February 5, 1990.
"Nonlinear Optical Effects in Molecular Materials and Polymers".
64. Hoechst-Celanese Corporation, February 21, 1990.
"Nonlinear Optics and Photonics with Molecular Materials and Polymers".
65. Michigan State University, Center for Fundamental Materials Research, February 23, 1990.
"Polymers for Electronics and Photonics".